

PATENT SPECIFICATION

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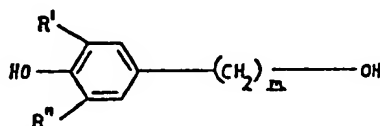
- (72) Inventors MAX EUGENE CHIDDIX and
 DAVID JAMES TRACY

(54) IMPROVEMENTS IN OR RELATING TO ESTERS OF -(3,5-DISUBSTITUTED-4-HYDROXYPHENYL) ALKANOLS AND THEIR USE AS STABILIZERS

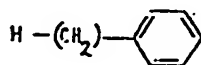
(71) We, GAF CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, having its main office at 140 West 51 Street, City, County and State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to esters of ω -(3,5-dialkyl-4-hydroxyphenyl)-alkanols with organic carboxylic acids and their use as stabilizers for organic materials subject to oxidative deterioration.

We have found that esters of ω -(3,5-dialkyl-4-hydroxyphenyl) alkanols of the general formula:



wherein R' and R'' each represent an alkyl group of 1—24 carbon atoms, an arylalkyl group (e.g.,



of 7—18 carbon atoms or a cycloalkyl group of 6—18 carbon atoms, and

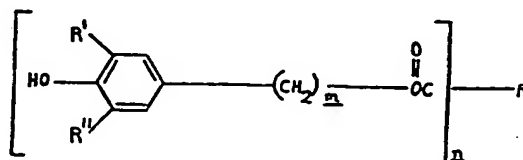
m represents an integer of from 2 to 10, with organic mono- and poly-carboxylic acids, having from 1 to 4 carboxyl groups, have superior antioxidant properties and are useful for stabilizing a variety of organic materials normally subject to oxidative and related deterioration, such as synthetic resins, plastics, elastomers, edible oils and fuels.

Many organic materials, such as lubricating oils, fuels, edible oils, elastomers, plastics, synthetic resins, etc., are adversely affected by oxygen giving rise to such undesirable results as formation of gum, discolouration, loss of physical properties such as tensile strength for resins or elasticity for elastomers, loss of potency, rancidity and/or odour formation. The prevention of oxidative deterioration and the extension of the useful life of such materials by the use of numerous types of oxidation inhibitors, has been described in a number of patent specifications and other technical literature. However, since by and large the various known antioxidants vary in their effectiveness, both

between the antioxidants themselves and the compounds in which they are used and the conditions to which the stabilized compounds are subjected, there is a continuous search for novel compounds which are useful as antioxidants.

The present invention provides novel compounds which are useful as antioxidants in a wide variety of organic compounds, and which with many organic compounds show an antioxidant effect which is equal or superior to that of known antioxidants. It further provides antioxidants which are less expensive to manufacture than many known antioxidants.

The esters of the present invention are represented by the following general formula:



wherein:

R', R'' and m are as defined above

R is an n valent organic radical which is the residue (preferably hydrocarbon) of an organic carboxylic acid having 1 to 4 carboxyl groups, the acid being either a saturated or unsaturated aliphatic (including cycloaliphatic) acid or an aromatic acid,

R may thus be an alkyl group of 1 to 25 carbon atoms, cycloalkyl group preferably of 6 to 18 carbon atoms, or an aryl or an arylalkyl group of preferably 6 to 18 carbon atoms, and

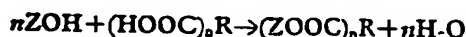
n is an integer of from 1 to 4.

The novel esters of the above general formula II may be prepared in a variety of ways from ω-(3,5-dialkyl-4-hydroxyphenyl)-alkanol of general formula I above and an organic carboxylic acid having 1 to 4 carboxyl groups or a derivative of such an acid such as the acyl chloride, anhydride or ester (preferably a lower alkyl (1—4 carbon atoms) ester).

For instance, the novel ester may be one wherein R' and R'' each represent an alkyl group having up to 8 carbon atoms and at least one of the said alkyl groups is branched on the *alpha* carbon atom or one wherein R represents the hydrocarbon residue of an aliphatic acid of 12 to 18 carbon atoms and n is 1.

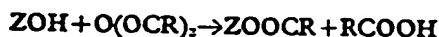
Convenient methods for the synthesis of the novel esters of general formula II above are outlined in Equations 1—4 below in which ZOH is used to designate the ω-(3,5-dialkyl-4-hydroxyphenyl)-alkanol of the general formula I above and n and R are as defined above. In these syntheses, suitable esterification catalysts such as mineral acids including sulphuric acid or such sulphonic acids as *p*-toluene-sulphonic acid may be employed if desired, and in case an acyl chloride of the organic acid is employed for the esterification, a suitable acid acceptor, such as pyridine, for the HCl which is generated is present. Such synthetic processes include; direct esterification as outlined in Eq. 1.

EQ. 1



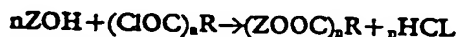
Reaction of the ω-(3,5-dialkyl-4-hydroxyphenyl)-alkanol with an acid anhydride, as outlined in Eq. 2.

EQ. 2



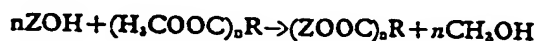
Use of an acyl chloride of the acid, as outlined in Eq. 3.

EQ. 3



or Ester interchange, preferably with a lower alkyl ester of the acid, such as the methyl esters, as outlined in Eq. 4.

EQ. 4



Suitable acids, which may be used as the free acid or in the form of their anhydrides, acyl chlorides or esters, in the production of the novel esters of the present invention include such saturated fatty acids as, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, caproic acid, isocaproic acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid and eicosanic acid; such unsaturated aliphatic acids as palitolic, olcic, ricinoleic, linoleic, linolenic, and erucic acids. By employing *alpha*, *beta*-unsaturated alkenoic acids of up to 8 carbon atoms, such as acrylic, methacrylic, vinyl acetic or allylacetic acids, polymerizable esters are obtained which can be used in a small amount as comonomer for the production of inter-polymers with other polymerizable ethylenically unsaturated monomers, to give internally stabilized copolymers. Where an ester of a higher aliphatic acid is desired we particularly prefer to use fatty acids of animal or vegetable origin such as tallow fatty acids, coconut oil fatty acids, soy bean fatty acids, rape seed acids, tall oil fatty acids, rosin acids, etc. either hydrogenated or unhydrogenated.

As examples of aliphatic dibasic acids may be mentioned; succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acids, and the polymers of fatty acids such as the dimers and trimers thereof of the type described by Bradley *et al.*, I and E. C. 33, 86—89 (1941).

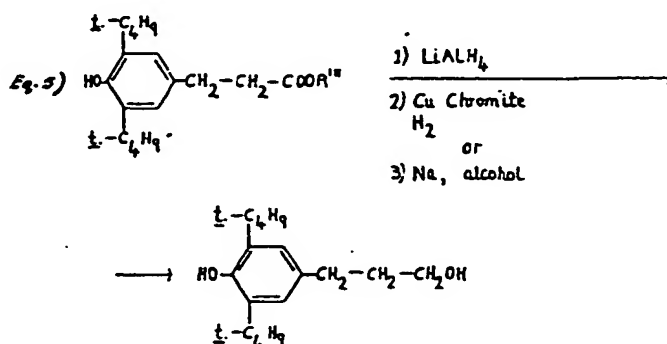
As examples of cycloaliphatic acids may be mentioned cyclohexane carboxylic acid, 1,2- and 1,4-cyclohexanedicarboxylic acid, naphthenic acids such as cyclopentanecarboxylic acid, cyclopentylacetic acid, 3-methylcyclopentylacetic acid, camphonanic acid, 4-methylcyclohexanecarboxylic acid and 2,4,6-trimethylcyclohexanecarboxylic acid, bicyclo(2,2,2)octa-5-ene-2,3-dicarboxylic acid and bicyclo(2,2,1)hepta-5-ene-2-carboxylic acid. As examples of aromatic carboxylic acids may be mentioned: benzoic acid, *o*-, *m*- and *p*-toluic acid, phthalic acid, terephthalic acid, hemimellitic acid, trimellitic acid, trimesic acid, prehnitic acid, mellophanic acid, pyromellitic acid, diphenic acid, 1-naphthoic acid, 2-naphthoic acid, naphthalene-1,8-dicarboxylic acid, naphthalene-1,4-dicarboxylic acid and naphthalene-1,4,5,8-tetracarboxylic acid. Also *o*-phenyl paraffinic acids such as phenylacetic, hydrocinnamic, phenylbutyric, δ -phenyl-*n*-valeric, E-phenyl-*n*-caproic, cinnamic, *o*-, *m*- or *p*-phenylene diacetic or *o*-phenyleneacetic- β -propionic acids.

As examples of (3,5-dialkyl-4-hydroxyphenyl)-alkanols which may be used to esterify the foregoing carboxylic acids may be mentioned:

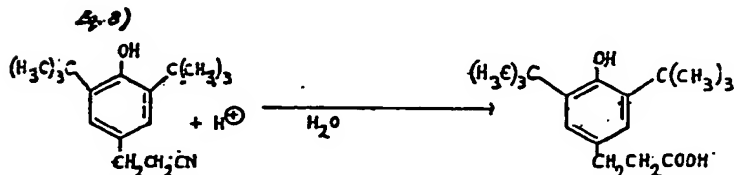
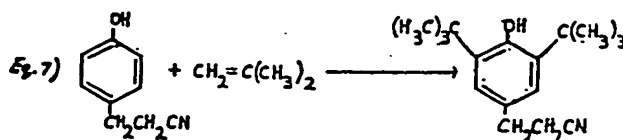
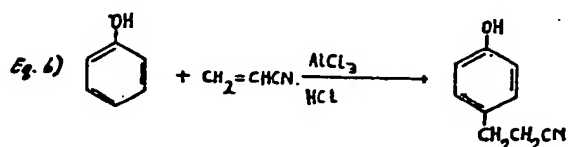
35	2-(3,5-dimethyl-4-hydroxyphenyl)-ethanol	
	2-(3-ethyl-5-methyl-4-hydroxyphenyl)-ethanol	
	2-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)-ethanol	35
	2-(3,5-dicyclohexyl-4-hydroxyphenyl)-ethanol	
	2-(3- <i>tert</i> -butyl-5-ethyl-4-hydroxyphenyl)-ethanol	
	2-(3-isopropyl-5-ethylphenyl-4-hydroxyphenyl)-ethanol	
40	2-(3,5-di- <i>tert</i> -octyl-4-hydroxyphenyl)-ethanol	
	2-(3,5-di- <i>tert</i> -dodecyl-4-hydroxyphenyl)-ethanol	40
	3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)-propanol	
	3-(3,5-dicyclohexyl-4-hydroxyphenyl)-propanol	
	3-(3,5-di- <i>sec</i> -octyl-4-hydroxyphenyl)-propanol	
45	3-(3- <i>tert</i> -octyl-5-isopropyl-4-hydroxyphenyl)-propanol	
	3-(3-methyl-5-hexylphenyl-4-hydroxyphenyl)-propanol	45
	3-(3-cyclohexyl-5- <i>tert</i> -butyl-4-hydroxyphenyl)-propanol	
	3-(3-methyl-5-bicyclohexyl[2,2,1]-4-hydroxyphenyl)-propanol	
	3-(3,5-dionyl-4-hydroxyphenyl)-propanol	
50	4-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)-butanol	
	4-(3- <i>tert</i> -butyl-5-isopropyl-4-hydroxyphenyl)-butanol	50
	4-(3- <i>tert</i> -butyl-5-ethylphenyl-4-hydroxyphenyl)-butanol	
	4-(3- <i>tert</i> -octyl-5-hexyl-4-hydroxyphenyl)-butanol	
	4-(3,5-di- <i>sec</i> -octyl-4-hydroxyphenyl)-butanol	
55	4-(3,5-di- <i>tert</i> -dodecyl-4-hydroxyphenyl)-butanol	
	5-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)-pentanol	55
	5-(3,5-di- <i>tert</i> -amyl-4-hydroxyphenyl)-pentanol	
	5-(3,5-di- <i>tert</i> -octyl-4-hydroxyphenyl)-pentanol	
	6-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)-hexanol	
60	6-(3,5-di- <i>tert</i> -amyl-4-hydroxyphenyl)-hexanol	
	8-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)-octanol	60
	8-(3,5-di- <i>tert</i> -amyl-4-hydroxyphenyl)-octanol and	
	10-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)-decanol	

While useful products are obtained by the use of ω -(3,5-dialkyl-4-hydroxyphenyl)-alkanols in which the alkyl groups in the 3 and 5 ring positions are either straight or branched chain; we particularly prefer to use those ω -(3,5-dialkyl-4-hydroxyphenyl)-alkanols in which at least one, and preferably both, of such alkyl groups is/are branched on its or their α carbon atom(s). Those compounds in which at least one and preferably both of the groups R' and R'' in formula II above, are a *tertiary* alkyl group—such as *t*-butyl, *t*-amyl, *t*-octyl or *t*-dodecyl are particularly preferred. In general, it appears that those compounds in which the phenolic hydroxyl group is afforded the most steric hindrance by the adjacent branched alkyl groups have the best antioxidant properties.

Suitable methods for synthesizing the above ω -(3,5-dialkyl-4-hydroxyphenyl)-alkanols include the method disclosed by S. Belostolskaya and V. V. Ershov, Izv. Akad. Nauk, SSSR Ser Khim (4)765(1964), Chemical Abstracts 61:2997c, for the production of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanol-1, by the reduction (with lithium aluminium hydride) of the 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanoic acid as outlined in Eq. 5 below. As indicated in Eq. 5, a lower alkyl ester of the acid may be employed if desired and in place of the use of LiAlH_4 reduction may be effected by refluxing with metallic sodium and an alcohol or by high pressure hydrogenation over a copper chromite catalyst for example. In EQ. 5 R''' represents hydrogen or lower alkyl (1—4 carbon atoms).



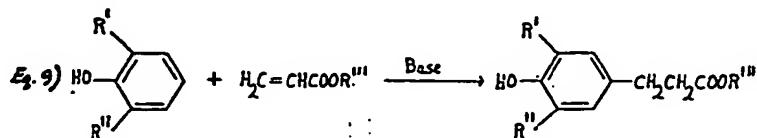
The 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoic acid, or an ester thereof, may be prepared by the series of reactions outlined in Eqs. 6, 7 and 8.



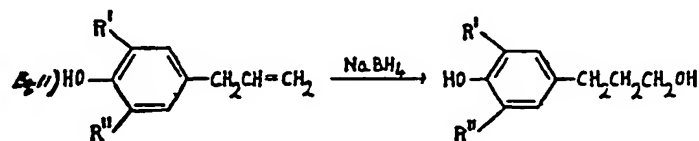
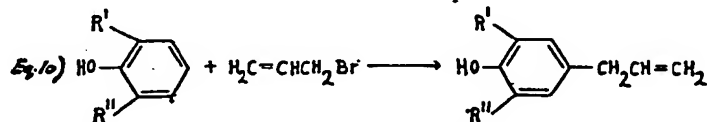
It will be apparent that by employing other olefins than isobutylene in the alkylation step outlined in Eq. 7 that the substituents in the 3 and 5 positions of the ring

may be controlled, thus by selection of the particular alkylating agent or alkylating agents ω -(3,5-dialkyl-4-hydroxyphenyl)-alkanols may be prepared in which R' and R'' in general formula I above are such groups as: methyl, ethyl, *n*-propyl, *isopropyl*, butyl, *isobutyl*, *t*-butyl, amyl, *t*-amyl, hexyl, octyl, *t*-octyl, decyl, nonyl, *n*-dodecyl, branched dodecyl, 2-ethyl hexyl, oxo-octyl, oxo-tridecyl, hexadecyl, octadecyl, behenyl, 1-methyl-cyclopentyl, cyclohexyl, dodecenyl, octadecenyl, oleyl, styryl, xylyl, tolyl, ethylphenyl, propylphenyl, hexylphenyl, octylphenyl, *n*-decylphenyl, *isodecylphenyl*, 1,1,3,3-tetra-methyl-*n*-butylphenyl, dodecylphenyl, octadecylphenyl, dioctylphenyl, didodecylphenyl, bicyclohexyl-(2,2,1), bicycloheptyl-(2,2,2) and bicyclohexenyl-(2,2,1).

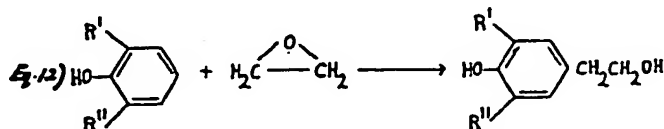
The ω -(3,5-dialkyl-4-hydroxyphenyl)-alkanoic acids and their esters may also be made by alkylation of a 2,6-dialkylphenol with an unsaturated acid or ester such as acrylic acid as outlined in Eq. 9.



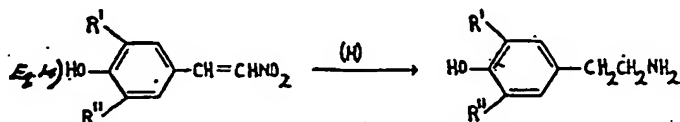
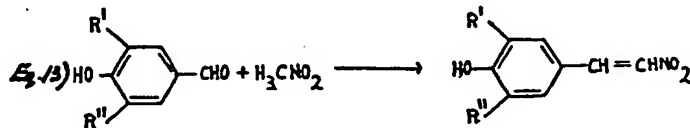
Another synthetic method from 2,6-dialkylphenols involves alkylation of the phenol with an alkylene halide as outlined in Eq. 10, followed by hydration of the double bond of the alkylene group thus introduced as by treatment with sodium borohydride as outlined in Eq. 11.

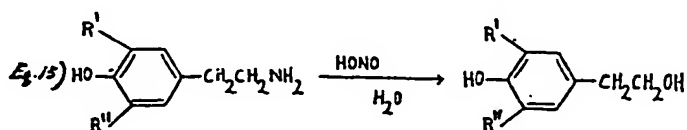


The 2-(3,5-dialkyl-4-hydroxyphenyl) ethanol may be produced by reaction of 2,6-dialkylphenol with ethylene-oxide under alkaline catalysis as outlined in Eq. 12.



or by the reaction of a 3,5-dialkyl-4-hydroxybenzaldehyde with nitromethane as outlined in Eq. 13, followed by reduction of the thus obtained product to the 2-(3,5-dialkyl-4-hydroxyphenyl)-ethylamine, as outlined in Eq. 14, followed by reaction with nitrous acid to form the alcohol, as outlined in Eq. 15.

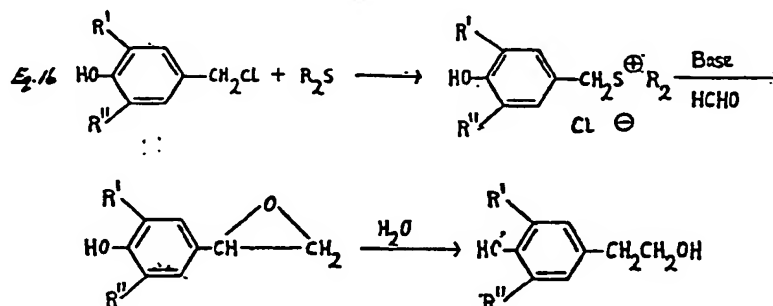




Alternatively it may be produced from a 3,5-dialkyl-4-hydroxybenzyl chloride by the series of reactions outlined in Eq. 16 by first reacting the benzyl chloride with a di-alkyl sulphide, followed by reaction with formaldehyde in the presence of a base to produce an epoxide which is then hydrolyzed to the alcohol.

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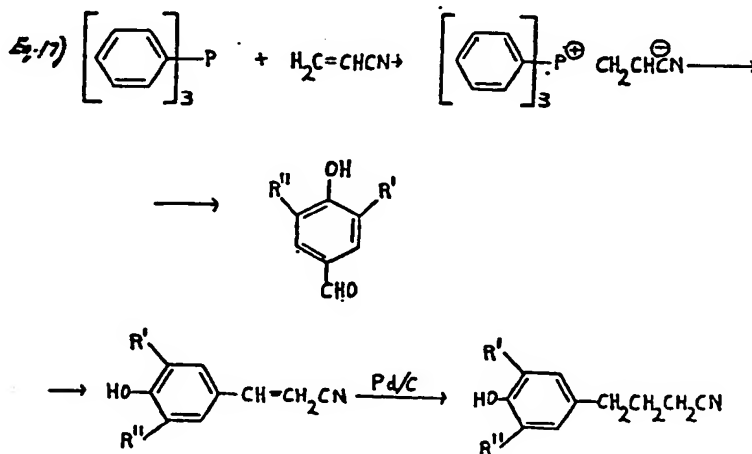
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Yet another method of synthesis of the ω -(3,5-dialkyl-4-hydroxyphenyl)-alkanols, involves the reaction of triphenylphosphine with an unsaturated nitrile, such as acrylonitrile, followed by reaction of the thus obtained intermediate with a 3,5-dialkyl-4-hydroxybenzaldehyde, and reduction of the thus obtained unsaturated nitrile to the corresponding saturated nitrile, by the series of reactions outlined in Eq. 17. The thus obtained saturated nitrile can then be hydrolyzed to the acid as outlined in Eq. 8 above, which may then be reduced to the desired alcohol as outlined in Eq. 5 above.

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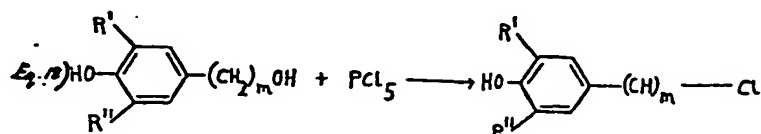
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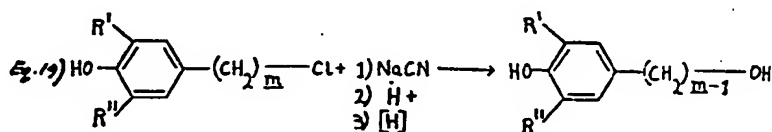


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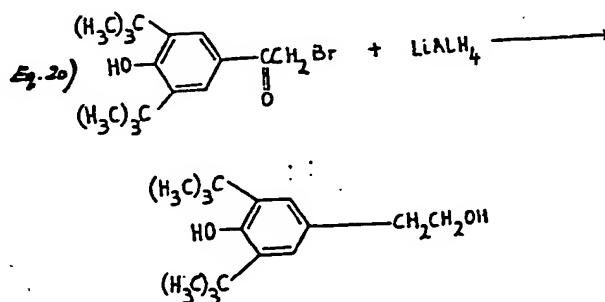
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It will of course be apparent that the carbon chain in the alkanyl group of the ω -(3,5-dialkyl-4-hydroxyphenyl)-alkanols may be increased by one carbon atom by converting the alcohol to the corresponding alkyl halide which may then be reacted with sodium or potassium cyanide, as outlined in Eqs. 18 and 19, respectively.





The preparation of 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl) ethanol by the reduction of a phenacyl halide, as outlined in Eq. 20, has recently been described (see L. Schwartz and R. V. Flor, *J. Org. Chem.*, 34, 1499 (1969).



It will be apparent that by selection of the particular ω -(3,5-dialkyl-4-hydroxyphenyl)-alkanol and the particular carboxylic acid with which it is esterified numerous novel esters of the general formula II above may be prepared, all of which are characterized by the presence in the molecule of from 1 to 4 hindered phenolic groups and having improved properties as antioxidants. The specific Examples which follow illustrate preferred methods for the preparation of certain of the preferred esters of this invention.

Preparation

Preparation of 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanol

To 250 ml. of diethyl ether under nitrogen was added

22.8 g. (0.6 mole) lithium aluminium hydride (Metal Hydride Corp.). To this slurry was added slowly at room temperature over a 4 hour period a solution of

91.8 g. (0.3 mole) 3,5-di-*tert*-butyl-4-hydroxyphenylpropionate ethyl ester in 150 ml. of diethyl ether. After the reaction was complete the excess hydride was destroyed with ethyl acetate and water. The product was neutralized with hydrochloric acid, washed with water, dried and concentrated. The solid obtained after crystallization from heptane melted at 66–67° (yield 85%).

Anal. Calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_3$: C, 77.22; H, 10.67.
Found: C, 77.19; H, 10.79.

Infrared: 3420–3380; 3640, ester carbonyl absent.

Example 1

Terephthalate ester of 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanol.

To 100 ml. of benzene was added

10.0 g. (0.04 mole) of 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanol and 3.9 g. (0.02 mole) of 1,4 phthaloyl chloride.

To the above solution was added over a 12 minute period at room temperature

3.0 g. (0.04 mole) of pyridine. The reaction mixture was heated to reflux for an additional 2 hours. A white solid was filtered off and the filtrate washed first with dilute hydrochloric acid and then water.

After drying (CaCl_2) and concentration

11.7 g. (90% of theory) of white solid (M.P. 125—126) was obtained. The infrared and nuclear magnetic resonance spectra agreed with the structure.

Anal. Calcd. for $C_{24}H_{28}O_6$: C, 76.58; H, 8.87; MW, 658
Found: C, 76.94; H, 9.14; MW, 565.

Example 2

Preparation of 1,2,4-Benzencentricarboxylate of 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanol
Employing the method of Example 1 using

10 39.6 g. (0.15 mole) 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanol-1
13.3 g. (0.05 mole) acid chloride of 1,2,4-benzene tricarboxylic acid
150 ml. of benzene and
11.9 g. (0.15 mole) of pyridine.

Yield:

15 44.5 g. viscous oil

Anal. Calcd. for $C_{46}H_{54}O_8$: C, 75.91; H, 8.92; MW, 949.
Found: C, 75.82; H, 9.48; MW, 830.

Example 3

20 Preparation of Stearate of 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanol
Water (1.8 ml.) was azeotroped from

26.4 g. (0.1 mole) 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanol
28.4 g. (0.1 mole) stearic acid,
300 ml. benzene, and
25 3.0 g. *p*-toluenesulphonic acid. The reaction mixture was washed with water,
dried over calcium chloride and concentrated yielding
46.6 g. (88%) of a white semi-solid. The infrared (ester at 1735 cm^{-1}) and
nuclear magnetic resonance spectra agreed with the structure.

Anal. Calcd. for $C_{44}H_{58}O_4$: C, 79.18; H, 11.77; MW, 531.
Found: C, 78.92; H, 11.53; MW, 550.

Example 4

30 Preparation of Bicyclic ester of 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)-
propanol

Substantially equimolar amounts

35 5.0 g. (0.02 mole) of 3,6 Endomethylene-1,2,3,6-tetrahydrophthaloyl chloride
(Aldrich) and
10.5 g. (0.04 mole) of 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanol-1 were
melted together on a steam bath and allowed to cool yielding a reddish
oil in 94% yield. The infrared spectrum showed the presence of an
ester carbonyl at 1725 cm^{-1} .

Example 5

40 Dimer acid ester of 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanol
Employing the method of Example 3 employing:

45 29.1 g. (0.1 eq.) Dimer acid ("Empol" 1022) ("Empol" is a Trade Mark for
a polymerized fatty acid; a C_{36} dibasic acid made by the dimerization
of polyunsaturated fatty acids.)
25.6 g. (0.1 mole) of 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propanol
1.5 g. *p*-toluene sulphonic acid
300 ml. benzene
azeotroped off
50 1.9 ml. water. The residue consisted of
49.5 g. dark oil which was the desired ester.

Anal. Mole Weight 994 Calcd.
Found: 880.

Infrared: 3650; 1740 cm^{-1} .

Example 6

Terephthalate ester of 3-(3,5-di-*tert*-amyl-4-hydroxyphenyl)-butanol-1
Using the method of Example 1,

- 5 12.2 g. (0.04 mole) of 3-(3,5-di-*tert*-amyl-4-hydroxyphenyl)-butanol-1 was
 esterified by reaction with
 3.9 g. (0.02 mole) of 1,4-phthaloyl chloride. 5
 12.0 g. of the named product was obtained as a white solid.

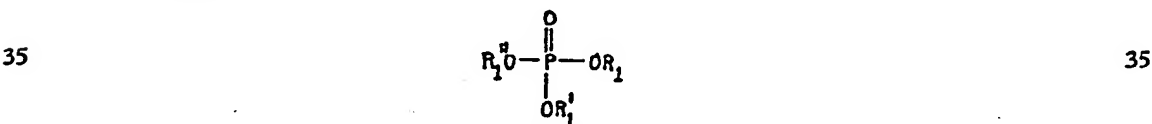
10 The novel esters of this invention find utility as antioxidants in a wide variety of
 organic materials subject to oxidative and related degradation. For example the present
 compounds show excellent antioxidant activity in synthetic resins, plastics, elastomers,
 edible oils, lubricating oils and fuels. 10

15 Among the examples of plastics that may be protected by the novel antioxidant
 compounds of this invention against oxidative degradation are included such poly-
 olefins such as poly(ethylene), poly(propylene), poly(butylene), poly(hexene-1), poly(4-
 methylpentene-1), poly(4-methylhexene-1), (poly(4,4-dimethylpentene-1), and copoly- 15
 mers of these olefin monomers such as poly(ethylene copropylene) and polymers of other
 polymerizable liquid ethylenically unsaturated monomers.

20 Other plastics and resins which may be protected against oxidation include poly-
 (styrene), poly(methyl styrene), poly(acrylates), poly(methyl acrylates), poly(ethyl
 acrylates), poly(2-ethylhexylacrylate), polycarbonates, polyesters such as polyethylene 20
 terephthalate, poly-phenylene oxide, polysulphones, polyimides, polybenzimidazoles,
 poly(acrylonitrile), poly(vinylchloride), polyvinylacetate, poly(ethylene oxide), poly-
 (propylene oxide), poly(methyl vinyl ether), poly(butyl vinyl ether), ketone-formaldehyde
 resins and indene resins.

25 Synthetic lubricants which can be protected include dialkyl oxalates, malonates, 25
 succinates, glutarates, adipates, pimelates, suberates, azelates, sebacates, esters from
 polyols such as pentaerythritol, trimethylol propane, and sorbitol, alkyl esters of aliphatic
 monocarboxylic acids such as lauric, oleic, palmitic, stearic and behenic acids. Other
 lubricants include silicone lubricants such as polysiloxane oils and greases of the type
30 poly-alkyl, polyaryl, polyalkoxy, polyaryloxy such as polydimethoxyphenoxy, siloxane, 30
 silicate ester oils such as tetraalkyloxy and tetraaryloxsilanes. Also fluorocarbon lubri-
 cants such as $(-\text{CF}_2\text{CFCl}-)_{n'}$ where n' =an integer, and polyalkylene glycol lubri-
 cants such as ethylene oxide-propylene oxide copolymers.

Phosphate ester lubricants such as



wherein R_1 , R_1' , and R_1'' represent hydrogen, phenyl, alkylphenyl or an alkyl radical
such as butyl, octyl, lauryl, oleyl and palmityl may likewise be protected.

40 Examples of elastomers which may be protected against oxidation include natural
 rubber, SBR rubber, GR-S rubber, GR-N rubber, poly-butadiene, cis-1,4-polyiso- 40
 prene, neoprene rubber, butyl rubber, nitrile and chloroprene.

45 Hydraulic fluids and lubricants, industrial oils, automatic transmission fluids, (or
 simple) transmission fluids, crankcase lubricating oils, transformer oils, turbine oils,
 cutting oils, gear oils, white oils, glass annealing oils, hydrocarbon waxes and vehicles
 for extreme-pressure lubricants may also be protected. Other lubricants include 45
 synthetic base greases formed by mixing a soap with an oil, soaps derived from animal
 and vegetable fats and oils, fatty acids, wool grease, rosin or petroleum acids, e.g.,
 lead oleate and lithium stearate.

50 Fuels which may be protected by the compounds of this invention include gasoline,
 jet fuel, diesel fuel, kerosine and fuel oil. 50

55 In addition to the above, commercial and edible fats and oils may be protected 50
 such as menhaden oil, cod liver oil, safflower oil, castor oil, soybean oil, olive oil, sesame
 oil, peanut oil, bebasau oil, palm oil, corn oil, oleomargarine, lard, butter, beef tallow,
 animal fat and hydrogenated shortening products such as "Spry", "Crisco" and "Snow-
 drift". "Spry", "Crisco" and "Snowdrift" are Trade Marks. Perfume oils and terpenes 55
 may also be protected. However, adequate safeguards and tests should first be carried
 out to be absolutely sure that any resultant compositions, intended for human or animal
 use, are not detrimental to humans or animals.

The novel compounds of the present invention may be added to the organic

material which is to be protected, in any manner. Simple intimate mixing or milling is frequently satisfactory. At other times the compounds of the present invention may be diluted with a mutual solvent for the organic material to be protected and then added to and mixed with it. The novel compounds of the present invention are usually present in an amount of from about 0.01 to 5 parts by weight of such compound per 100 parts by weight of the organic material.

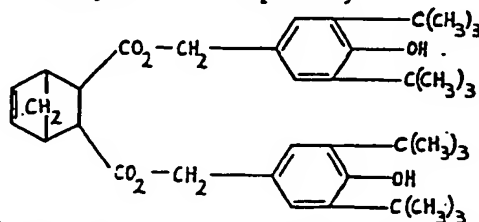
The effectiveness of the novel compounds of this invention as antioxidants is illustrated by the following specific Examples of their use.

Example 7

To illustrate the antioxidant effect of the products of this invention in protecting polypropylene, the standard oven oxidation test was used.

The antioxidant compound under test is compounded into unstabilized polypropylene on a Banbury type laboratory mill (Brabender Plastograph) at 183°C. for 10 minutes. A 40 mil thick sheet of compounded material is compression moulded on a laboratory press ("Carver") using 245°C. platen temperatures, 10,000 lbs. pressure on the 2-1/4 in. diameter ram, and a dwell time of 2 minutes. "Carver" is a Trade Mark. The sheets are air cooled under pressure before removal from the press. Standard microdumbell specimens (ASTM D 1708-59T) are die cut from the sheet. The specimens are suspended vertically in an air circulating oven operating at 300°F. Time to initial failure is noted as exposure time required for first signs of micro-cracking or crazing of specimen. Time to final failure is noted as the exposure time required to produce breaking of the specimen when flicked with the finger.

For purposes of comparison the results obtained in this test with two esters of 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol and with "Ionol", a well known commercial hindered phenol antioxidant (2,6-di-*tert*-butyl-4-methylphenol), are also given in Table I below. "Ionol" is a Trade Mark. The benzyl esters used were the diester of norbornene dicarboxylic acid (formula III below) and the acetic acid ester disclosed in Example VI of U.S. patent specification 3,116,305; they are identified in table I as "Benzyl ester A" and "Benzyl ester B" respectively.



The results obtained in this test, when using the products of the foregoing Preparation and Examples 1-4 at a concentration of 0.5 part thereof per 100 parts of polypropylene are summarized in Table I.

TABLE I

Additive	Conc. (phr)	Hours to Failure
Product of the Preparation	0.5	11
Product of Example 1	0.5	1040
Product of Example 2	0.5	586
Product of Example 3	0.5	178
Product of Example 4	0.5	670
Product of Example 6	0.5	110
"Ionol"	0.5	9
Benzyl Ester A	0.5	12
Benzyl Ester B	0.5	12
None	—	7

(phr means parts per hundred)

Example 8

The great value of this invention in providing increased antioxidant protection for lubrication oils is illustrated by the results obtained in the Rotary Bomb Oxidation Test (ASTM D 2272-64T). In this test 50 g. of test oil, 5 ml. of distilled water and 10 ft. of No. 14 AWg electrolytic copper wire wound in a coil with an outside dia. of 50 to 52 mm. are placed in a glass container. The glass container is then inserted in a chrome plated copper bomb and covered with a watch glass. Five ml. of distilled water is also added to the bomb to aid heat transfer when the bomb is placed in the heating

bath. The bomb is then closed and sealed. A pressure gauge is attached. The bomb is charged with oxygen to 90 p.s.i. and allowed to stand for 10 minutes to check for any leaks. The bomb is then placed on rotating stand in a heating bath, kept at 150°C. The bomb is tilted to 30° from the horizontal and rotated at 100 rpm. Within 10 to 15 minutes the contents of the bomb increases from 90 p.s.i. to about 180 to 190 p.s.i. due to expansion of O₂. The pressure of the bomb remains at this level for a certain time, the length of time depending on the effectiveness of the oxidation inhibitor in the test oil formulation, and then starts to drop. The period from the time when the maximum pressure is attained to the time when the pressure has dropped by 25 p.s.i. from the maximum pressure, is reported as induction period and serves as a measure for the effectiveness of the oxidation inhibitor. The oil used for this test in this and the remaining Examples was a solvent refined paraffinic oil having the following properties.

	Gravity °API 32.2	
	Kinematic Visc. cst.	
15	100°F—103	15
	210°F—39.5	
	VI—95	
	Pour pt. °F.—10	
	Flash pt. °F.—380	
20	Colour ASTM—0.5	20
	Fire °F.—430	
	Neutralization Value—Nil	
	Cu Corrosion 212°F.—Neg.	

The results are summarized in Table II.

25	TABLE II			25
	Additive	Conc. (%)	Induction Time (Min.)	
	Product of Example 3	0.5	80	
	Product of Example 4	0.5	58	
30	Product of Example 6	0.5	45	30
	Base Oil		25	
	(no additive)			

The lifetime of the oil is increased by a factor of from 2 to 3.

Example 9

In order to demonstrate the increased protection against oxidation, provided by the novel esters of this invention, for liquid fuels such as catalytically cracked gasoline, the standard ASTM-D-525-55 test was used.

50 cc of test gasoline in a glass container is put into a stainless steel bomb and charged with O₂ to attain the pressure of 100 psi. A pressure gauge is attached to the bomb. The whole assembly is placed into boiling water.

Break point for the experiment is reached when a pressure drop of 2 psi. is observed in 15 minutes and in a subsequent 15 minutes a pressure drop of more than 2 psi.

This time is taken as the induction period.

Physical Data of the Gasoline (a catalytic gasoline) Used:

45	API, Gravity, °F:	49.7	45
	Distillation, Initial BP:	108°F.	
	5%	134	
	10%	148	
50	20%	168	50
	30%	192	
	40%	224	
	50%	258	
	60%	292	
55	70%	324	55
	90%	358	
	90%	396	
	95%	416	
	End Point:	432	
	Recovery, %:	98%	
60	Reid Vapour Pressure (100°F.):	5.1 lbs.	60

Reid Vapour Pressure is the vapour pressure of a liquid determined at 100°F and expressed in pounds per square inch.

The oxidation stability afforded to this catalytically cracked gasoline is demonstrated by the data summarized in Table III.

5

TABLE III

5

Additive	Concentration (%)	Induction Time (min.)
Product of Example 3	0.05	525
Product of Example 1	0.05	355
None	0.05	315

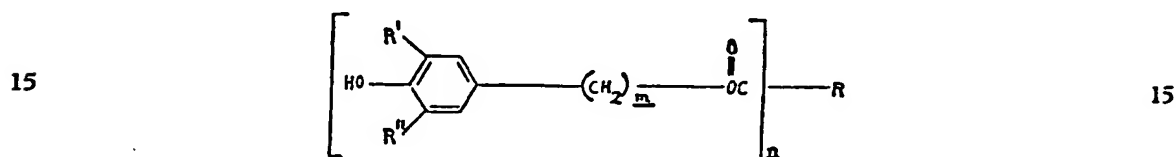
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10

The products of this invention increase dramatically the oxidative lifetime of gasoline.

WHAT WE CLAIM IS:—

1. An ester characterized by the general formula:



15

15

wherein:

R' and R'' each represent an alkyl group of 1—24 carbon atoms, an arylalkyl group of 7—18 carbon atoms or a cycloalkyl group of 6—18 carbon atoms,

R represents an alkyl group of 1—25 carbon atoms, a cycloalkyl group of 6—18 carbon atoms, an aryl group of 6—18 carbon atoms or an arylalkyl group of 7—18 carbon atoms and is *n* valent,

m represents an integer of from 2 to 10 and

n represents an integer of from 1 to 4.

2. An ester according to Claim 1, wherein

R' and R'' each represent an alkyl group having up to 8 carbon atoms and at least one of the said alkyl group is branched on the *alpha* carbon atom.

3. An ester according to Claim 1 or Claim 2, wherein

R represents the hydrocarbon residue of an aliphatic fatty acid of 12 to 18 carbon atoms and

n is 1.

4. An ester according to Claim 1 or Claim 2, wherein

R represents the hydrocarbon residue of a dimer acid and

n is 2.

5. An ester according to Claim 1 or Claim 2 wherein

R represents the hydrocarbon residue of an aliphatic dicarboxylic acid.

6. An ester according to Claim 1 or Claim 2, wherein

R represents the residue of an aromatic acid.

7. A compound according to Claim 1, which is the terephthalate ester of 3(3,5-di-*tert.* butyl-4-hydroxyphenyl)-propanol.

8. A compound according to Claim 1, which is the 1,2,4-benzenetricarboxylate ester of 3(3,5-di-*tert.* butyl-4-hydroxyphenyl)-propanol.

9. A compound according to Claim 1, which is the stearate ester of 3-(3,5-di-*tert.* butyl-4-hydroxyphenyl)-propanol.

10. A compound according to Claim 1 which is 3,6-endomethylen-1,2,3,6-tetrahydrophthalate ester of 3-(3,5-di-*tert.* butyl-4-hydroxyphenyl)-propanol.

45

11. A composition stabilized against oxidation, consisting essentially of an organic compound normally subject to oxidative degradation and a minor effective antioxidant amount of the compound as set forth in any one of Claims 1 to 10.

5 12. An ester according to Claim 1 substantially as set forth and described herein-before.

13. A composition according to Claim 11 substantially as herein described and exemplified.

5

MEWBURN ELLIS & CO.,
Chartered Patent Agents,
70—72 Chancery Lane,
London W.C.2.
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